Physics 53

Thermal Physics 1

Statistics are like a bikini. What they reveal is suggestive; what they conceal is vital.
— *Arthur Koestler*

Overview

In the following sections we will treat macroscopic systems that are in **thermal equilibrium**. Most of our discussion will center on the behavior of gases. We will use appropriate macroscopic variables, some of which are already familiar, such as density, volume and pressure.

We will usually assume the CM of the system is at rest, and that molecular velocities are randomly distributed as to direction, so there is no bulk flow or velocity field to consider. There may be energy (kinetic or potential or both) internal to the molecules themselves, if they are not monatomic.

The total kinetic energy of the random molecular motion, plus any energy the molecules may have internal to themselves, constitutes the **internal energy** of the system. This is one of the new macroscopic variables we will use in our description.

Thermal equilibrium, temperature and the Zeroth Law

Macroscopic variables used to describe the state of a system in thermal equilibrium are called **state variables**. Density, volume and pressure are state variables, as is internal energy. We will introduce two more as we go along: temperature and entropy.

What is meant by thermal equilibrium is this:

If the system is in thermal equilibrium, state variables all have definite values.

Since the state variables all represent averages of some kind, what it means to have a "definite value" is that the *fluctuations* which might make the average uncertain are small enough to be ignored. In a statistical situation, such fluctuations are generally inversely proportional to the number of particles. In systems of macroscopic size that number (roughly Avogadro's number) is extremely large, so the fluctuations are tiny.

Most of the possible situations a system may be in are *not* states of thermal equilibrium. Nevertheless, it is an experimental fact that **a system left to itself evolves toward thermal equilibrium**. (How that happens is still not fully understood in detail.) The

time it takes for a non-equilibrium state to evolve to equilibrium is called the "relaxation time". It varies from case to case, but is often quite short by human standards.

Two macroscopic systems can exchange energy with each other. This exchange can be accomplished by collisions among particles at a common interface, or by other methods such as emission and absorption of electromagnetic radiation. If energy exchanges can take place, we say the systems are in **thermal contact**. Such exchanges generally disrupt, at least temporarily, the states of equilibrium of the two systems. It may happen, however, that two systems brought into thermal contact undergo no disruption of equilibrium in either system. Then we say *the systems are in equilibrium with each other*.

The properties of this "mutual thermal equilibrium" constitute a fundamental law:

Zeroth Law of thermodynamics	If systems A and B are both in thermal equilibrium with system C, then they are also in equilibrium with each other.

This principle is the basis for the state variable called **temperature**. Two systems in equilibrium with each other are said to have the same temperature. If two systems with different temperatures are brought into thermal contact, there is exchange of energy until they come to mutual equilibrium at the same (new) temperature.

Temperature is a scalar quantity. It is defined operationally by its measurement, using a device called a *thermometer*. When this (small) device is placed in thermal contact with the (large) system in question, some energy is exchanged between the two. (Because the thermometer is small, this energy exchange does not change appreciably the state of the large system.) Some physical aspect of the thermometer (for example, the length of a column of liquid) changes in an observable way on account of the energy exchange; when this aspect stops changing we know the system and the thermometer are in equilibrium. By calibrating the changes in the thermometer one makes a scale of temperatures. The first thermometer and scale was made by Fahrenheit around 1700.

How is temperature related to average behavior of the microscopic states? We will find that temperature is one measure of the average energy of (random) motion of the molecules in the system.

The ideal gas law

For a gas the most commonly used state variables are pressure (P), volume (V) and temperature (T). For reasons to be made clear later, the temperature of a gas is usually specified using a scale with the lowest possible temperature chosen as zero. The most popular of these scales is that due to Lord Kelvin (William Thomson), which has 100

units ("Kelvins", denoted by K) between the ice point and the steam point of water. In this scale the "absolute zero" of temperature is approximately 273 K below the ice point.

Pressure, volume and temperature are not all independent of each other. An equation relating them is called an **equation of state**. It is generally written in the form $T = f(P,V)$. Much research has been done to find the function $f(P,V)$ appropriate to particular gases.

In the late 17th century it was found that for a wide variety of gases, at conditions of pressure and temperature easily obtainable in the technology of that time, there is a simple and universal function that describes them all. It is $f(P,V) = (\text{const}) \cdot PV$. This formula is called the **ideal gas law**.

In SI units, it is usually written in either of two equivalent forms:

Ideal gas law	$PV = NkT$
	$PV = nRT$

In the first form N is the number of molecules in the gas and k is a universal constant, called Boltzmann's constant, which in SI units is $k = 1.38 \times 10^{-23}$. The second form specifies the quantity of gas in terms of the number of moles n, and R is the "universal gas constant". $R = 8.31$ in SI units.

The two forms are related through Avagadro's number N_A, the number of molecules per mole. We have $N = nN_A$ and so $R = N_A k$. Experimentally $N_A \approx 6.02 \times 10^{23}$.

The ideal gas law is an approximation that gives good results for gases that are not very dense, at temperatures and pressures near those in which we live.

Internal energy

The **internal energy** of a system, denoted by E_{int}, consists of the total energy of random motion of the particles, plus any energy associated with internal structure of the particles, such as rotation and vibration about their individual CM.

The notation given here for internal energy is not standard; more commonly it is denoted by U. We use a notation that avoids confusion with potential energy, since internal energy also includes the kinetic energy of random motion of the molecules of the system.

In terms of the average energy E_{av} of the particles, $E_{\text{int}} = NE_{\text{av}}$, where N is the total number of particles. Since E_{av} generally depends on the temperature, E_{int} depends on T. For an ideal gas it depends *only* on T.

In general, both of these energies *increase* with increasing T.

The internal energy of a system can be changed by transfers of energy in or out of the system, which can be accomplished by a variety of methods. Two are of special importance:

- The system can be put into thermal contact with another system at a different temperature. Energy will be transferred from the system whose particles have higher average energy (higher T) to the one with lower average energy (lower T). The energy transferred this way is called **heat**, denoted by Q, and the process is called *heat flow*. We will discuss later some of the details of this kind of process.

- Energy can be transferred through **work** done by external forces. If external forces do *positive* work on the system, then (assuming no other energy transfers are occurring) the internal energy *increases*. If the system does positive work on something external to it then the internal energy decreases.

An example of work done is the motion of a piston in a cylinder filled with gas. If an external force pushes the piston inward to reduce the volume, the internal energy of the gas increases. If the gas expands, pushing the piston outward against the external force, the internal energy of the gas decreases.

The First Law of thermodynamics

The energy balance in this situation is described by an important law:

First Law of thermodynamics	If heat dQ is taken into a system, while the system does work dW, then the internal energy of the system changes by the amount $dE_{\text{int}} = dQ - dW$.

Although all the quantities in this law have the dimensions of energy, they have quite different meanings:

- Heat and work are *energy in transit*, not energy a system "possesses". They are *not* state variables. The amount of heat flow or work done in changing the state of the system depends not only on the initial and final states of the system, but *on what process was used* to make the change.

- Internal energy, on the other hand, *is* a state variable. The change of internal energy depends *only* on the initial and final states of the system, not at all on the process.

The logical content of the 1st law is often described as the assertion that internal energy exists and is a state variable.

Thermal processes

A given change in internal energy can result from many different combinations of heat flow and work done. Each such combination is a different thermal process. There are a few simple processes of importance in our analysis:

Constant volume	For a gas, this usually means $dW = 0$.
Constant pressure	If the volume changes by dV, then the work done *by* the system is $dW = PdV$.
Isothermal	Constant temperature. If E_{int} depends only on T, then $dE_{int} = 0$ and $dQ = dW$. This is the case for an ideal gas.
Adiabatic	No heat flow: $dQ = 0$.

Specific heats

If heat flows into a system its temperature increases — unless the system loses as much energy through work done as the heat flow brings in, or unless a change of phase (discussed below) is taking place. The amount of heat necessary to raise the temperature by one unit (in SI units, 1 K) is called the **heat capacity** of the system, denoted by C.

Clearly this depends on how large the system is (how many particles it contains) as well as what kind of substance is involved. To eliminate the dependence on quantity it is common to define the heat capacity for a unit quantity of matter. This is called the **specific heat** of the substance, denoted by c.

Heat capacity and specific heat both depend on the *process* by which the heat is taken in. One often attaches subscripts to the symbols to denote the process used. For example, if the volume is kept constant, the specific heat is denoted by c_V. If the pressure is kept constant we have c_P.

The general definition of specific heat is

Specific heat	$c_{(process)} = \dfrac{1}{(\text{quantity})}\left(\dfrac{dQ}{dT}\right)_{(process)}$

For a gas it is common to use the number of *moles* to measure the quantity, and the specific heat is then the heat capacity per mole (often called the *molar* heat capacity).

For solids or liquids it is more common to use the mass as the measure of quantity.

In practice, one often rewrites the definition of *c* in the following manner:

$$(dQ)_{\text{(process)}} = (\text{quantity}) \cdot c_{\text{(process)}} \cdot dT$$

This allows for easy use in conjunction with the 1st law.

Changes of phase

When a substance melts, changing from solid to liquid, we say its **phase** has changed. The strong bonds of a solid have been converted into the weaker interactions of nearest neighbors in a liquid. This requires input of energy.

Similarly, when a liquid boils or evaporates, becoming a gas, the interactions between particles have been almost completely eliminated, so input of energy is again required.

The input energy needed to make these **phase changes**, without changing the temperature, is called the **latent heat**. It is denoted by L_f for the case of melting ("fusion") and L_v for the case of vaporization. It is generally specified per unit mass of the material, so the amount of heat necessary to make the phase change takes the form

$$Q = mL,$$

where *m* is the mass of the substance in question.

Specific heats of an ideal gas

We have mentioned the specific heats of a gas for the cases of constant pressure and constant volume. In the ideal gas approximation, there is a simple relation between these quantities.

From the 1st law it follows that if the volume is kept constant (no work is done) then $dQ_V = dE_{\text{int}}$. Since from the definition of c_V we have $dQ_V = nc_V\,dT$, we find a very useful relation for ideal gases:

$$dE_{\text{int}} = nc_V dT.$$

Since both of the variables in this equation are state variables, **this is a general relation**, independent of the process. It allows us to write a very useful form of the 1st law that applies to ideal gases:

First Law for ideal gas	$dQ = nc_V dT + dW$

Despite the appearance of c_V in this relation, it holds for *any* process, not just one at constant volume.

Now consider input of heat dQ at constant pressure. This is related to c_P by

$$dQ = nc_P dT.$$

But if the pressure is constant, then we have from the ideal gas law that

$$nRdT = d(PV) = PdV = dW.$$

The 1st law then gives

$$dQ_P = dE_{\text{int}} + dW, \text{ or } nc_P dT = nc_V dT + nRdT.$$

This reveals a simple relation between the specific heats:

Specific heats of ideal gas	$c_P = c_V + R$

Adiabatic Processes for Ideal Gases

In an adiabatic process $dQ = 0$, so the 1st law says that $dE_{\text{int}} + dW = 0$.

For an ideal gas, $dE_{\text{int}} = nc_V dT$ and $dW = PdV$. Using the ideal gas law we see that

$nRdT = d(PV) = PdV + VdP$. Using $c_V = c_P - R$ and a little algebra, we have

$$\frac{c_P}{c_V}\frac{dV}{V} + \frac{dP}{P} = 0.$$

Introducing the notation $\gamma = c_P / c_V$ and integrating, we have $\gamma \ln V + \ln P = \text{const.}$ This give the ideal gas formula for adiabatic processes:

Adiabatic process for ideal gas	$PV^{\gamma} = \text{const., where } \gamma = c_P / c_V$

P-V diagrams

We have seen that for a gas only two of the variables P,V,T are independent. This means that a point on a plot of P vs. V (called a **P-V diagram**) corresponds to a definite value of T as well. In dealing with equilibrium states of a gas, it is thus sufficient to specify such a state by a point on a *P-V* diagram.

If the system moves to a different equilibrium state, the point on the *P-V* diagram correspondingly moves. If the process by which the change was made involves only infinitesimal changes such that all the intermediate states are also equilibrium states, then we can plot the process as a continuous curve on the *P-V* diagram.

This would actually require the process to be infinitely slow, so we are dealing with a mathematical idealization, which gives a good approximation in many cases. It is called the "quasi-static" approximation.

If the volume of the gas changes by dV while pressure P is applied, then the work done *by* the gas is $dW = P\,dV$. For a finite change in volume the work is given by

$$W(a \rightarrow b) = \int_a^b P\,dV .$$

Here a and b represent equilibrium states, and thus points on the *P-V* diagram.

The work done by the gas is the area under the curve on a *P-V* diagram.

It is *positive* if the volume *increases*.

In many applications we will be interested in repetitive processes such that the system returns to its original state. These are **cyclic** processes. If such a process is quasi-static, the curve representing it on the *P-V* diagram is a *closed* curve, and the total work done per cycle is the area *enclosed by* the curve.

The special processes listed earlier are represented by curves on the P-V diagram.

Constant pressure is represented by a horizontal line.

Constant volume is represented by a vertical line. No work is done.

Isothermal (T = constant). For an ideal gas we find $P = (\text{const.})/V$. This is a hyperbola on a *P-V* diagram, asymptotic to the axes.

Adiabatic ($dQ = 0$). We found earlier that for this process involving an ideal gas, $PV^\gamma = \text{const.}$, where γ stands for the ratio c_P/c_V. On a *P-V* diagram this is similar to the isothermal curve, but it has steeper slope since $\gamma > 1$.

The figure below shows these curves.